Experimental Report

01/02/2006

Proposal: **5-26-174** **Council:** 4/2005

Title: Texture analysis of misfit layer cobaltite ceramics

This proposal is a new proposal

Researh Area: Materials

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Samples: Bi2Ca2Co2Ox and Ca3Co4O9

Instrument	Req. Days	All. Days	From	To
D1B	3	3	01/08/2005	04/08/2005

Abstract:

Thermoelectric (TE) power generation has the potential to provide a new energy source in the next few decades. The recent discoveries of large thermopower coexisting with low electrical resistivity in cobaltite layered structures such as NaxCoO2, Bi2Sr2Co2Ox and Ca3Co4O9, opened the way to the exploration of new oxide thermoelectric materials and the development of polycrystalline bulk materials for potential applications.Due to their high structural anisotropy, the alignment of plate-like grains by mechanical and/or chemical processes is necessary to attain macroscopic properties comparable to the intrinsic crystallographic ones.The texture analysis is consequently required to quantify the degree of orientation of the materials and to establish a clear relationship elaboration-microstructure-texture-properties.The neutron investigations (D1B or D20 line) avoid the defocusing effect occuring in X-ray diffraction, provide a whole volume analysis and permit an equivalent diffraction of all (hkl) crystallographic planes for each chi orientation. These points represent the motivation of our proposal.

Textured $Ca_3Co_4O_9$ thermoelectric oxides by thermoforging process

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Using thermoforging process, dense $Ca_3Co_4O_9$ (Co349) thermoelectric oxides have been successfully textured. The various parameters influencing the formation of the Co349-textured material have been investigated. The electrical transport measurements show an anisotropy of the resistivity in good agreement with scanning electron microscopy observations. Texture is quantified by neutron-diffraction measurements and correlated to anisotropic resistivity measurements and Seebeck coefficients. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2120892]

INTRODUCTION

In contrast to the skutterudite compounds, there exists only few reports on processing and application of thermoelectric oxide materials. In spite of a limited effort, the misfit thermoelectric materials are now emerging as potential candidates for high-temperature devices. Some works have been devoted to the development of processing bulk thermoelectric oxides and the search for compounds[1–6] with high figures of merit. Besides these oxides themselves, their preparation with satisfactory structural homogeneity, material density, and grain alignment are essential for the design of practical systems suitable for applications such as power generation. Especially, the optimization of platelet orientation is one of the main problems to overcome. Weak links at grain boundaries and low sample density, which affect the resistivity and consequently the figure of merit, are two reasons for improving the texturing technique.[7] The figure of merit is defined as $\mathrm{ZT}=S^2T/\rho\kappa$, with S being the Seebeck coefficient, T the temperature, ρ the electrical resistivity, and κ the thermal conductivity, and varies by six orders of magnitude[5,8,9] in the literature. These differences are assumed to be related to the microstructures resulting from the use of different types of process: (i) conventional or spark plasma sintering,[10] (ii) reactive templated grain growth,[6] (iii) hot pressing,[7,11] and (iv) magnetic texturation.[12]

In this paper, we report the results obtained on the polycrystalline $Ca_3Co_4O_9$ (Co349) thermoelectric oxide processed by thermoforging. This process allows to form the bulk textured materials having a good connection between the platelets in order to decrease the transport resistivity. The correlation between the microstructures and texture with the thermoelectric properties is investigated.

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EXPERIMENT

The $Ca_3Co_4O_9$ powder was prepared by conventional solid-state reaction. Pure Co_3O_4 and $CaCO_3$ were mixed, calcined (900 °C, 12 h), and pressed uniaxially (30 MPa) into pellets. The samples were processed into the versatile setup using the thermomechanical schedule described in more detail elsewhere.[13] Briefly, the pellet is heated at 920 °C for 24 h under various stresses (0–16 MPa) in air. For the microstructural analysis of the nonpressed and hot-forged samples, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS) were used. The chemical specimen composition after processing and the texture of the samples were investigated using x-ray diffraction (XRD) measurements on a Philips apparatus with Cu $K\alpha$ radiation and neutron diffraction using the D1B setup (Institut Laue-Langevin, Grenoble, France), respectively. Electrical resistivity was measured using a dc four-probe method using the Quantum Design PPMS system, a homemade high-temperature device, and a steady-state technique for Seebeck measurements, respectively. The measurements were performed in the temperature range from 5 to 700 K in self-field.

RESULTS AND DISCUSSION

Figure 1 shows cross-section SEM micrographs of the samples processed at 0, 7, and 16 MPa. The microstructure of the hot-pressed dense samples shows homogeneously distributed platelet-shaped (>15 μm) grains in contrast to the nonpressed sample where one can clearly observe some voids and platelet-shaped grains (5 μm). It can be seen that with increasing applied stress from 0 to 16 MPa, the grain size increased from 5 to >15 μm. Crystallite growth has been favored by hot forging as illustrated by the microstructures. In other words, crystallite growth is easier at larger stresses that improve grain contacts. These observations are

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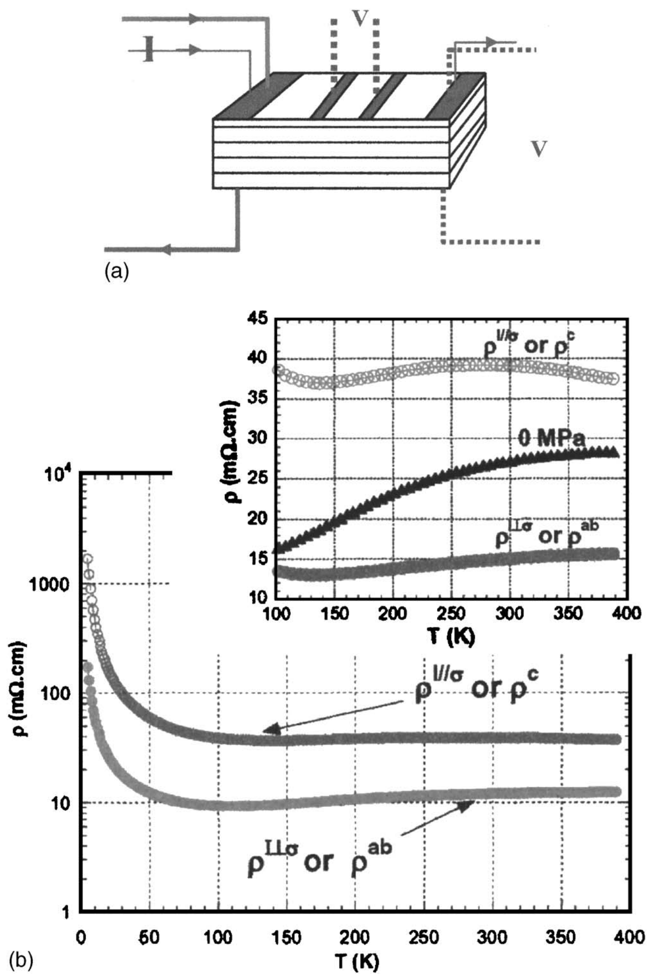

FIG. 3. (a) Sketch of the geometry used for measuring resistivity. (b) Temperature dependence of the resistivity ρ for current applied parallel (○) and perpendicular (●) to the stress (σ=7 MPa) axis. (Inset) High magnification above room temperature showing the nontextured sample (▲ σ) between both configurations.

The temperature dependence of the Seebeck coefficient for the in-plane hot-forged (σ=16 MPa) samples is illustrated on Fig. 4. We can notice the positive values confirming the p-type conductor behavior. At room temperature the magnitude of S=125 μV/K obtained can be compared with the data reported in the literature.[5,6,12] The same sample has been measured at high temperatures (inset Fig. 4). The thermopower value above 120 μV/K is clearly confirmed.

Quantitative texture analysis of the anisotropic sample has been investigated using neutron-diffraction measurements. The texture data [Fig. 5(a)] show very strong intensity variations when the sample is tilted relative to the neutron beam. The combined analysis of the neutron data[15] indicates that the {00ℓ} orientation is the unique component of texture as reported by Guilmeau *et al.*,[7] with comparable texture strengths.

The texture is axially symmetric around the stress axis, giving rise to the {00ℓ} cyclic fiber texture. Figure 5(b) illustrates the achieved texture degrees at the intermediate (7 MPa) and largest applied pressure (16 MPa) using {004} pole figures. The maximum orientation density on these figures are around 3.9 and 16.8 multiple of a random distribution (mrd) with 33% and 23% of the volume randomly oriented, respectively.

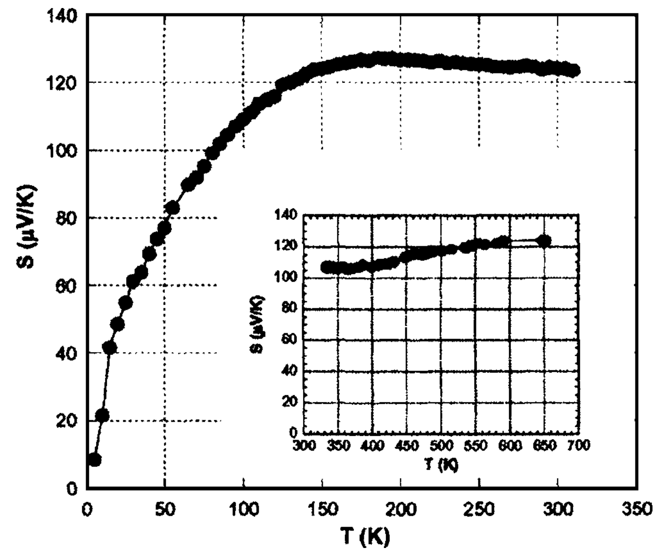

FIG. 4. Seebeck coefficient vs temperature for the hot-forged (σ=16 MPa) sample. Inset: Above room-temperature measurements.

CONCLUSIONS

In summary, the thermoelectric oxide $Ca_3Co_4O_9$ bulks have been processed using a thermoforging technique. The pellets obtained are highly dense and strongly oriented with the mean c axis parallel to the stress direction applied during the heat treatment. Crystallite alignment of the bulk sample is confirmed by the strong texture as seen from the neutron-diffraction measurements and corresponds to the grain orientation as seen by the SEM measurements. The effect of thermomechanical processing is clearly evidenced by $\rho(T)$ curves. The resistivity decreases with increasing applied

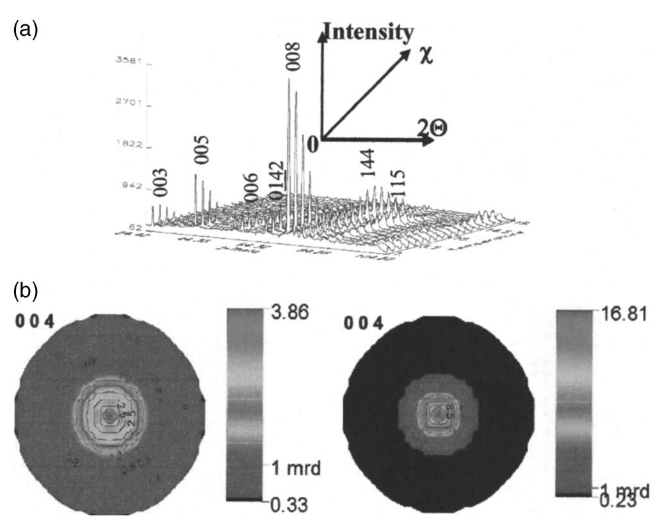

FIG. 5. (a) Neutron-diffraction diagrams measured at different tilt angles of the sample, which show the presence of a strong texture. (b) {004} pole figures for the samples processed at 7 and 16 MPa (left and right, respectively) as extracted from Fig. 5(a) using the combined approach. The stress axis is perpendicular to the pole figure plane.